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(54) **Suspension, coating, agglomeration and uses of imidoperoxycarboxylic acids.**

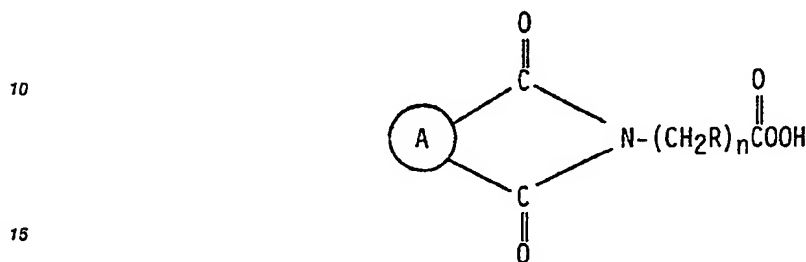
(57) The present patent application discloses the suspension in aqueous media and the suspension coating and agglomeration of imidoperoxycarboxylic acids, the use of imidoperoxycarboxylic acid-containing suspensions and coated agglomerates as bleaching agents, as well as the use of imidoperoxycarboxylic acids in soaking detergents and in dishwashing detergents for automatic dishwashing machines.

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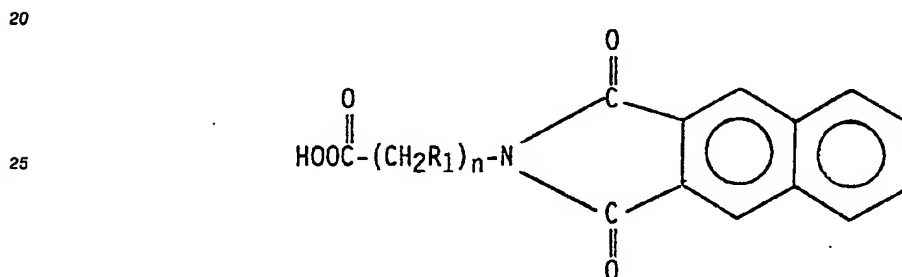
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SUSPENSION, COATING, AGGLOMERATION AND USES OF IMIDOPEROXYCARBOXYLIC ACIDS

The present invention relates to the suspension in aqueous media and the suspension coating and agglomeration of imidoperoxycarboxylic acids, the use of imidoperoxycarboxylic acid-containing suspensions and coated agglomerates as bleaching agents, as well as the use of imidoperoxycarboxylic acids in overnight soaking detergents, and in dishwasher detergents for automatic dishwashers. These imidoperoxycarboxylic acids are represented by the following general formula:



wherein A is a substituted or unsubstituted benzene ring or naphthalene ring, or



$n=1-10$ and R and R_1 may be the same or different and are selected from hydrogen and a C_1-C_4 carboxylic acid radical.

Several of these imidoperoxycarboxylic acids, including ϵ -N-N-phthaloylamino-peroxycaproic acid (PAP), are known as bleaching agents from a publication entitled, "TAED and New Peroxycarboxylic Acids as Highly Efficient Bleach Systems," 80th AOCs Meeting, Cincinnati, OH, May, 1989 (TAED publication). This article also mentions other known bleaching agents such as magnesium-monoperphthalic acid (H-48) and dodecanediperacid (DPDA). From the article it is clear that PAP exhibits different properties than either H-48 or DPDA. In addition, European patent numbers 0 325 288 and 0 325 289 also disclose such materials and their use in bleaching.

Aqueous suspensions of DPDA are known for use as pourable bleaching compositions from EP 0 176 124. This patent publication also discloses a method for making these aqueous suspensions of DPDA. Another form of DPDA suspension useful as an aqueous liquid bleaching composition is disclosed in EP 0 160 342. This patent publication also teaches a method for making aqueous DPDA suspensions.

European Patent Publication 0 254 331 discloses a process for the preparation of agglomerates containing DPDA and their use in bleaching compositions. Typically, the agglomerates are made with linear alkyl benzene sulphonate as the surfactant.

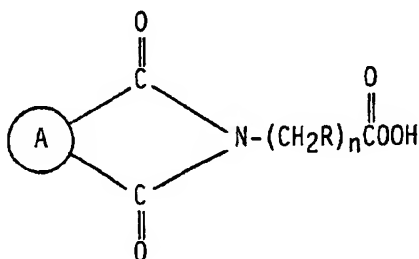
European Patent Publications 0 300 461 and 0 300 462 disclose certain heterocyclic peroxycarboxylic acids and their use as bleaching agents. In all cases, these heterocyclic peroxycarboxylic acids include quaternized nitrogen atoms.

Australian Patent Publication 39286/85 discloses a process for the overnight soaking of textiles in order to clean these textiles. The overnight soaking agent typically contains a bleaching agent and at least one bleach activator to enhance the effect of the bleaching agent. In this patent, an activator comprising phthalic anhydride and N-acetyl-phthalimide is disclosed.

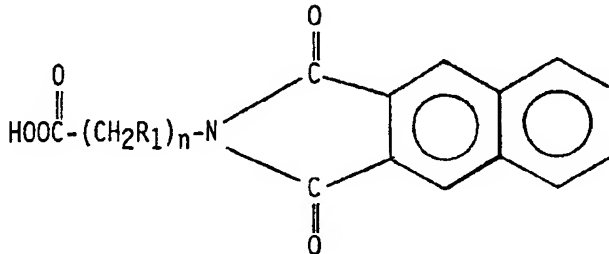
The present imidoperoxycarboxylic acid(s) (IPCA) can be synthesized by the process disclosed in the TAED publication, the disclosure of which is hereby incorporated by reference. One only needs to select

the appropriate phthalimido alkanic acid to provide the desired product. In this process, phthalic anhydride is reacted with ϵ -caprolactam with heating to achieve a quantitative yield of phthalimidocaproic acid. Then, the phthalimidocaproic acid is oxidized in acid solution in the presence of 35-50% hydrogen peroxide to produce the IPCA which, being almost insoluble in the reaction system, is isolable by filtration. After drying, the IPCA is obtained in good yields. In addition, materials such as N-Phthaloyl-DL-glutaminic acid anhydride may be peroxidized to produce the IPCA used in the present invention. Further, other acid anhydrides such as naphthalene-1,4,5,8-tetracarboxylic acid anhydride and 1,8-Naphthalic acid anhydride may be used as starting materials to produce IPCA useful in the present invention.

The present invention relates to the suspension in aqueous media and the suspension agglomeration of IPCA, the use of IPCA-containing peroxydicarboxylic acid-containing suspensions and agglomerates as bleaching agents, as well as the use of IPCA in overnight soaking detergents. These IPCA are represented by the following general formula (I):



wherein A is a substituted or unsubstituted benzene ring or naphthalene ring, or



$n=1-10$ and R and R_1 may be the same or different and are selected from hydrogen and a C_1-C_4 carboxylic acid radical.

More particularly, the present invention relates to a pourable, aqueous bleaching composition including a suspended IPCA of the formula I and an alkali metal salt of an alkyl benzene sulphonic acid. The present invention also includes the use of these aqueous suspensions as pourable bleaching compositions, and packaged bleaching compositions comprising these suspensions.

The present invention also relates to a process for coating IPCA particles and preparing agglomerates containing an IPCA of the formula I. In the process, an aqueous suspension of said IPCA is agitated in the presence of at least 25% by weight of a water-impermeable material at a temperature above the melting point of said water-impermeable material but below the decomposition temperature of said IPCA. The obtained coated and agglomerated particles are then cooled with continued agitation to a temperature at which the water-impermeable material solidifies and the resulting coated materials are isolated. Further, the invention relates to shaped particles, solid bleaching compositions and pourable bleaching compositions comprising coated IPCA.

Further, the present invention relates to the use of an IPCA of the formula I as a bleaching component or an activator in an overnight soaking detergent composition and to a process for cleaning textiles by soaking them for a period of at least 4 hours in an aqueous wash liquor including a detergent, and an IPCA of the formula I.

Finally, the present invention also relates to the use of an IPCA of the formula I as a bleaching component or activator in a dishwashing detergent for automatic dishwashing machines and to a process for washing dishes employing a composition containing at least one IPCA of the formula I.

The bleaching component in the present invention is an imidoperoxycarboxylic acid represented by the formula I. The present suspensions, agglomerates and overnight soaking compositions may contain one or mixtures of two or more imidoperoxycarboxylic acids within the formula I. The preparation of these acids can be carried out in a known manner such as is described in the TAED publication, the disclosure of which is hereby incorporated by reference. In general terms, phthalimidoalkanoic acid is oxidized in acid solution in the presence of 35-50% hydrogen peroxide to form the nearly insoluble peracid which may then be isolated by, for example, filtration. After drying, the acid is obtained in good yields.

It has been found, in the development of the present invention, that pourable, aqueous suspensions of imidoperoxycarboxylic acids of the formula I which include an alkali metal salt of an alkyl benzene sulphonic acid are surprisingly more stable than similar suspensions of the known bleaching agent DPDA. Similarly, it was also found that suspensions of the acid in accordance with the present invention additionally including a surfactant material are significantly more stable than similar suspensions of DPDA. In addition, other aqueous suspensions may be made containing both a thickening polymer and a thinning polymer as suspending agents.

Generally, the suspensions according to the present invention contain the imidoperoxycarboxylic acid in an amount sufficient to provide an active oxygen content of the suspension of between 0.05 and 5% and more preferably between 0.1 and 3%.

The present suspensions must contain an alkali metal salt of an alkyl benzene sulphonic acid. The alkyl group may be branched or linear and contains 9 to 22 carbon atoms, preferably 9 to 15 carbon atoms and most preferably 11-13 carbon atoms. As examples of these alkyl benzene sulphonates may be mentioned sodium undecyl benzene sulphonate, sodium dodecyl benzene sulphonate and sodium tridecyl benzene sulphonate. Mixtures of these salts of alkyl benzene sulphonates may also be employed. It is most preferred that the suspensions in accordance with the present invention contain sodium dodecyl benzene sulphonate.

The alkali metal salt of the of the alkyl benzene sulphonic acid should be used in an amount such that the suspension is pourable and physically stable. In this regard, the amount of imidoperoxycarboxylic acid may also be adjusted to improve the pourability of the suspensions. For example, lower concentrations of the acid will generally render the suspension more easily pourable. Generally, the composition will contain the alkali metal salt of the alkyl benzene sulphonic acid in an amount of 0.5 to 40% by weight, and more preferably from 2 to about 20% by weight, calculated on the weight of the composition. Use of amounts less than 0.5% by weight may result in compositions that have insufficient physical stability and use of amounts above 40% by weight may produce viscous suspensions having a tendency to gel and become unpourable or may create significant safety hazards.

The alkali metal salts of alkyl benzene sulphonic acids which are commercially available are so-called technical products which generally include, as an impurity, an inorganic salt such as sodium sulphate. These technical products, as well as substantially pure salts, may be used in making the suspensions of the present invention. The addition of inorganic salts, it has been found, has a favourable impact on the physical stability of the present suspensions. In particular, these inorganic salts tend to prevent precipitation.

Thus, the suspensions of the present invention also include an inorganic salt in an amount of from 0.1 to 35% by weight and, more preferably, 2 to 10% by weight, calculated on the weight of the suspension. Concentrations of inorganic salts about 20% by weight are generally only employed in order to achieve a density match between the solution density and the peroxide density. The preferred inorganic salts are sodium sulphate, potassium sulphate and mixtures thereof. The total inorganic salt in the composition may be added as a separate component, may be derived solely from the inorganic salts present as impurities in the alkali metal salts of alkyl benzene sulphonic acids or be derived both from the alkali metal salts and by being added as a separate component. In addition, it has been found that increasing the amount of the inorganic salt in the suspension will allow a reduction in the amount of alkali metal salt of alkyl benzene sulphonic acid without a substantial effect on the properties of the suspension. This is advantageous in practice since the inorganic salt is far less costly than the alkali metal salt of an alkyl benzene sulphonic acid.

The compositions of the present invention may contain other additives such as surfactants, thickening agents, sequestering agents and builders, for example. Surfactants useful in the present invention include anionic, nonionic, cationic, zwitterionic, soapy surfactants or mixtures thereof. Preferred surfactants are anionics, nonionics and/or soapy surfactants.

The anionic surfactants comprise alkyl aryl sulphonates, alkyl sulphates, alkyl ether sulphates, alkane and alkene sulphonates and other similar materials. In these surfactants, the alkyl radicals may contain from 9-20 carbon atoms and numerous anionic surfactants are listed in Schwartz, Perry, Vol. II, 1958,

"Detergents and Surface Active Agents," the disclosure of which is hereby incorporated by reference. Other suitable anionic surfactants include sodium lauryl sulphate, potassium dodecyl sulphate, sodium salt of lauryl polyoxyethylene sulphate, dioctyl ester of sodium sulphosuccinic acid and sodium lauryl sulphate.

Suitable non-ionic surfactants include ethylene oxide and/or propylene oxide condensation products with alcohols, alkylphenol, fatty acids, and fatty acid amides. These products have 5 to 30 ethylene oxide and/or propylene oxide groups. Fatty acid mono- and dialkylamides and tertiary amine oxides may also be used. Specific examples of these materials are nonyl phenol polyoxyethylene ether, tridecyl alcohol polyoxyethylene ether, dodecyl mercaptan polyoxyethylene thioether, and 12-15 carbon fatty alcohol ethoxylates.

Cationic surfactants include quaternary ammonium salts having a 12-20 carbon alkyl group, such as, for example, stearyl dimethyl benzyl ammonium chloride, dicoco dimethyl ammonium chloride, cetyl pyridinium chloride, and other known cationic surfactants.

Zwitterionic surfactants include alkyl- β -iminodipropionate, alkyl- β -aminopropionate, fatty imidazolines, betaines and mixtures thereof. Specific examples include 1-coco-5-hydroxyethyl-5-carboxymethyl imidazoline, and N-dodecyl-N,N-dimethyl amino acetic acid.

The total amount of surfactant in the suspensions of the present invention may vary from 0 to 50% by weight and more preferably 2 to 35% by weight.

Suitable thickening agents are described in GB 1 535 804, the disclosure of which is hereby incorporated by reference. In addition, other thickening agents such as Xanthan gum, Welan gum, Rhamsan gum and Alpha flo [®], a succinoglycan polysaccharide, are also useful in the present suspensions. Thickeners can be used up to amounts at which the suspension remains pourable.

Sequestering agents which bind stray metal ions which may accelerate the decomposition of the peroxide bleaching component include ethylene diamine tetraacetate, sodium pyrophosphate, phosphoric acid, dipicolinic acid and organic phosphonic compounds like hydroxy ethylidene diphosphonic acid and amino tri(methane phosphonic acid). These agents may be employed in amounts of 0.01 to 1% by weight of the suspension.

Builders such as polycarboxylates may be employed in the present compositions. Further, minor amounts of optical brighteners, perfumes and organic solvents may be present.

The present bleaching suspensions may be employed, for example, in the pre-washing treatment of textiles at low temperatures up to 60 °C, or they may be added as a separate, liquid component to the wash liquor along with the usual heavy and light duty detergents.

The suspensions of the present invention may be prepared by adding the imidoperoxycarboxylic acid, with stirring, to a mixture of water, an alkali metal salt of an alkyl benzene sulphonic acid, an inorganic salt and any other desirable additives. The imidoperoxycarboxylic acid may be used in the form of a powder preferably having a primary particle size of 1-100 μ m, or in the form of a wet filter cake such as that obtained during the preparation of the imidoperoxycarboxylic acid. The pH of the final suspension may be adjusted, if desirable, for the particular application in which the suspension is to be used. It has been found that the imidoperoxycarboxylic acids are more effective as bleaching agents at lower pH than at a pH of, for example, 11.

It has also been found that imidoperoxycarboxylic acids, when used as a bleaching component, often result in a high incidence of pin-point spotting. Pin-point spotting is a phenomena whereby the textile treated with the bleaching component acquires a number of tiny white spots thereon as a result of contact with the bleaching component. Of course, pin-point spotting is a serious problem since it damages the color and aesthetic appearance of textiles. Accordingly, the present invention has for another of its objects, to provide agglomerates of imidoperoxycarboxylic acids which prevent or substantially reduce the incidence of pin-point spotting. In addition, the use of such a coating must not detract from either the stability of the acid or from its bleaching activity.

The coating and agglomeration of bleaching agents containing peroxy acids in an aqueous medium is an important procedure since it is known that peroxy acids are hazardous materials, particularly when handled in solid or highly-concentrated forms. The present process provides a relatively simple and safe way of coating and agglomerating imidoperoxycarboxylic acids for use in bleaching compositions.

The coating and agglomeration of the imidoperoxycarboxylic acid is carried out in an aqueous suspension of the acid. Aqueous suspensions prepared by the above-described methods may be used or, more simply the coating and agglomeration may be directly carried out in the aqueous suspension obtained when preparing the imidoperoxycarboxylic acids by reaction of imidocarboxylic acids with hydrogen peroxide as described herein. The second process offers several useful advantages including the elimination of the difficult filtration step in the preparation process, and the immediate desensitization of the imidoperoxycarboxylic acid by coating thereby eliminating the necessity of handling the peroxy acid in solid

or concentrated form. Further, the direct coating and agglomeration of the material simplifies the processing and thereby reduces costs. As is known in the art, sulphuric acid may be present during the peroxy acid preparation process to provide in situ desensitization of the acid. For the present peroxy acids this is generally unnecessary, however, if such desensitization is to be used, the sulphuric acid content of the resulting suspension should not exceed 50% by weight, calculated on the total amount of sulphuric acid and water.

The amount of imidoperoxycarboxylic acid which should be present in the starting suspension is generally in the range of 2 to 20% by weight, preferably 5 to 20% by weight and most preferably 10 to 18% by weight, calculated on the weight of the total suspension. The peroxy acid particles in the suspension preferably have a diameter of 0.5 to 100 μm and even more preferably 0.5 to 50 μm .

Water-impermeable materials suitable for use in the present process should have a melting point in the range of 30-80°C and more preferably 40-60°C. Generally these materials are selected from the fatty acids, fatty alcohols and fatty esters. Preferred fatty acids are those containing 10 to 20 carbon atoms, such as stearic acid. The most preferred of this group are fatty acids having 12 to 14 carbon atoms such as lauric acid and myristic acid. As fatty alcohols may be used compounds having 14 to 20 carbon atoms including tetradecanol, 1-hexadecanol, and 1-octadecanol. Also, mixtures of acids and mixtures of alcohols may be employed. These fatty acid esters are derived from monoalcohols as well as from polyols such as tallow fat.

The water-impermeable material should be used in an amount of from 30 to 100% by weight of the peroxy acid. When less than 30% by weight is employed, the agglomerates are difficult to isolate from the suspension, the agglomerates exhibit insufficient storage stability, and the problem of pin-point spotting may not be completely eliminated. Amounts above 100% by weight of water-impermeable material may impair the bleaching activity of the resulting agglomerates. The most preferred range for the water-impermeable material is from 33 to 70% by weight.

The temperature of coating and agglomeration is above the melting point of the water-impermeable material and below the decomposition temperature of the peroxy acid. Typically temperatures below about 90°C will be employed and usually it is safer and simpler to choose a coating and agglomeration temperature which is only a few degrees above the melting point of the water-impermeable material. The present process may be carried out in standard equipment using standard stirring and isolating techniques.

The size of the resultant agglomerates may be varied by altering the process variables, for example a higher stirring rate will produce smaller granules. It is recommended that the agglomerates have a maximum diameter of 5-3000 μm , more preferably 5-2000 μm and most preferably 5-1000 μm . The coated agglomerates may optionally be dried in the usual manner.

The coated agglomerates may be further processed into shaped particles including an additional, hydratable material. A preferred hydratable material is an inorganic salt which is not alkaline in aqueous solution. Examples of such salts are NaH_2PO_4 and $\text{KAl}(\text{SO}_4)_2$. Sodium sulphate is the most preferred hydratable material.

The shaped particles may be in a variety of shapes and generally have a reduced active oxygen content as compared to the agglomerates thereby rendering the material safer for handling and transport. These particles may have a maximum dimension of 50 to 4000 μm or, more preferably, 50 to 2000 μm . The shaped particles may be made by making a pasty material at a temperature above the hydration temperature of the hydratable material from the coated agglomerates, the hydratable material, water and optional additives. This pasty material is then broken up into particles of the desired size and shape and cooled to a temperature below the hydration temperature of the hydratable material. Finally, the particles are dried. The hydratable material will generally comprise 1 to 10 parts by weight based on the weight of the shaped particles in their anhydrous state.

The coated agglomerates and shaped particles prepared by the process of the present invention may be used as a bleaching component in a solid, particulate textile laundry detergent and bleaching composition. Such compositions generally contain 1-40% by weight of the bleaching component and 60-99% by weight of the components commonly employed in detergents. Such additives are listed in detail herein as optional additives to the suspensions of the present invention.

The coated agglomerates may also be employed as part of an aqueous, pourable bleaching composition or of detergent and bleaching compositions for cleaning textiles. In such compositions the coated agglomerates are employed in a suspended state and may be suspended, for example by the suspension method of the present invention. These pourable compositions may also find utility as disinfectants in some applications.

The present invention also encompasses the use of imidoperoxycarboxylic acids as the bleaching agent or activator in soaking detergents. Such soaking detergents are well known in the art and are most

frequently employed in developing countries where electricity and washing machines are not so common. In general, enough of the imidoperoxycarboxylic acid will be employed to provide an active oxygen content in the wash liquor of from 1 ppm to about 50 ppm. More preferably, ranges of about 10-30 ppm are employed. It has been found that with imidoperoxycarboxylic acid lower active oxygen contents will produce equivalent or better cleaning than with the present commercial products. Thus, the use of these imidoperoxycarboxylic acids in soaking detergents provides a significant advantage over the present state of the art.

Along the same lines, the present invention also includes a process for the cleaning of textile materials by soaking the textile materials for a period of at least four hours in an aqueous wash liquor comprising water, a soaking detergent composition and an imidoperoxycarboxylic acid, and rinsing said textile materials. Such processes are known in the art with other activators and the soaking detergents are well known compositions. These soaking detergents may optionally contain an additional enzymatic cleaning agent to enhance the cleaning ability of the wash liquor. Such enzymatic cleaning agents are particularly useful for cleaning things like blood.

The present invention further includes dishwashing detergents for automatic dishwashing machines containing a bleaching agent comprising the IPCA, the present invention and the use of such a bleaching agent in dishwashing detergent for automatic dishwashing machines to wash dishes. Numerous dishwashing detergents are known. However, it has surprisingly been found that IPCA is more compatible with many of the key ingredients in dishwashing detergents than other peroxy bleaching agents such as DPDA.

A typical dishwashing formulation uses chlorine bleaches which generally have the disadvantage that they may produce chlorine-containing compounds which are found in the dishwashing waste water and may be pollutants. The present materials overcome this advantage since they contain no chlorine. Commercial dishwashing detergents based on sodium metasilicates are described in, "Sodium Metasilicates, Raw Materials for Dishwashing Detergents", O. Sörensson, Tenside Detergents 23, (1986) the disclosure of which is hereby incorporated by reference.

Dishwashing detergents may also be made with sodium disilicate hydrate as well.

The present invention includes these dishwashing detergent formulations with 0.1-20% of peroxyacid bleaching agent IPCA and, optionally a small percentage of a surfactant. The preferred form of the IPCA is as a solid such as, for example, a granulate. More preferably, the dishwashing compositions contain 0.5-10% of the peroxyacid bleaching agent.

The process for washing dishes is simply to use a dishwashing detergent in the standard manner, said dishwashing detergent including IPCA in the bleaching component.

The following examples are presented to further illustrate the present invention.

Example 1

Preparation of 6-Phthalimido Peroxyhexanoic Acid

In a stirred, two liter, double walled peroxidation reactor the following materials were sequentially added: 389 g. hydrogen peroxide (70% solutions, $t = 20^\circ \text{C}$); 166 g. distilled water ($t = 20^\circ \text{C}$); 1384 g. of concentrated sulfuric acid (95.6%, ambient temperature); and the contents were then cooled down to a temperature of 20°C .

Next, 523 g. of 6-phthalimido hexanoic acid of 99% assay was dosed in regular intervals over a 60 minute period. The contents of the reactor were retained at 20°C and stirring was continued for a second one hour period. It was observed that the organic acid dissolved easily into the reaction mixture. The first peroxy acid crystals began to precipitate 15 minutes after the final dosing of the 6-phthalimido hexanoic acid.

The precipitation of the peroxy acid was completed upon the addition of the peroxy reaction mixture to a stirred reactor comprising 4900 grams of water. The precipitates were collected by filtration on a 20 cm. diameter filter. Residues of the reaction mixture were removed from the crystals by washing with water several times. The final wet cake comprised 45% of 6-phthalimido peroxyhexanoic acid of a purity of about 98% and about 55% of water. The yield was calculated to be 95% based on the peroxyacid.

Example 2

Preparation of Stable Bleach Suspensions

Bleach suspensions were prepared by the incorporation of dried peroxyacid powder into liquid carrier. 6-phthalimido hexanoic acid having an active oxygen content of 5.50% was employed. The suspensions were prepared as follows.

The liquid carrier is prepared first simply by mixing the ingredients as shown in table 1. In this case two different liquid carriers according to the present invention were prepared, namely 2a and 2b. In example 2a, a liquid carrier was prepared with water, sodium lauryl alkyl sulphonate and sodium sulphate. In example 2b the liquid carrier additionally included a fatty alcohol ethoxylate. Next, a portion of the liquid carrier is admixed with the dried peroxyacid powder manually to form a paste. Then, the remainder of the liquid carrier is admixed with the paste until the desired suspension is obtained. Of course, the suspension process is carried out at a temperature in excess of the melting point of the sodium lauryl alkyl sulphonate but well below the decomposition temperature of the peroxyacid.

The resultant suspension is then poured into polyethylene bottles which were closed and stored at 40°C over a several week period. The residual peroxyacid content was determined at regular intervals as the active oxygen content in order to determine the storage stability of the suspensions. The results are shown in table 1.

Comparative Example 1

The same procedure was followed as in example 2 except that instead of 6-phthalimido hexanoic acid, DPDA was employed having an active oxygen content of 11.50%. Accordingly, a reduced amount of DPDA was used in order to provide suspensions having the same initial active oxygen content as were prepared in example 2. The storage stability was measured for comparative purposes and was found to be significantly worse than the storage stability for the 6-phthalimido hexanoic acid suspensions over a 2 week period. The results are shown in table 1 and are listed as examples C1a and C1b.

Table 1

Example	2a	C1a	2b	C1b
Type of peroxyacid	PAP	DPDA	PAP	DPDA
Composition (in % by weight)				
PAP	9.1	-	9.1	-
DPDA	-	4.4	-	4.4
LAS	6	6	6	6
Fatty alcohol ethoxylate	-	-	3	3
Sodium sulfate	10	10	7	7
Water	balance		balance	
STABILITY 2 Weeks at 40°C				
Residual Peroxy Acid (in % of Initial Active Oxygen Content)	86	63	72	63

PAP = 6-phthalimido hexanoic acid
LAS = Sodium lauryl alkyl sulphonate

Example 3

Preparation of 6-Phthalimido Peroxy Hexanoic Acid Coated With Lauric Acid

The coating operation was conducted in a double-walled 6 liter reactor provided with a turbine stirrer. 900 grams of the wet cake described in preparation example 1 above was suspended in 2.5 liters of water. The content of the reactor was heated to 45°C. 142 grams of lauric acid (assay 95%, t=50°C) was admixed over a 5 minute period. The temperature of the reaction vessel was raised to 50°C and the suspension was maintained at 50°C for an additional one hour period and then cooled to 20°C over a 15 minute period. The solids were separated by filtration. 877 grams of solids were recovered consisting of 37.6% water, 46.8% organic peracid and 15.6% lauric acid coating.

Example 4

To establish the behavior of agglomerates prepared by the process of the present invention with regard to pin point spotting, tests were carried out on two standard test fabrics, viz. an Immidial Black test fabric from EMPA (Switzerland) and Sunak test fabric from TNO (Netherlands). In the tests use was made of a standard detergent, IEC detergent, of the following composition:

- 8% sodium linear alkyl (average C_{11.5}) benzene sulphonate,
- 2.9% ethoxylated (14 Ethylene oxide units) tallow alcohol,
- 3.5% sodium soap (13-26% C₁₂-C₁₆; 74-78% C₁₈-C₂₂),
- 43.7% sodium triphosphate,
- 7.5% sodium silicate (SiO₂: Na₂O = 3.3:1),
- 1.9% magnesium silicate,
- 1.2% carboxymethyl cellulose,
- 0.3% sodium tetraethylene diamine tetraacetate,
- 0.3% optical brightener (stilbene type),
- 21% sodium sulphate, and
- 9.7% water.

The tests were conducted as follows, use being made of agglomerates containing 25 and 40% by weight of lauric acid, calculated on the 6-phthalimido peroxyhexanoic acid, and prepared in a manner analogous to that described in example 3 above.

A circular-cut piece of test fabric 9.4 cm in diameter was placed on the bottom of a beaker having an internal diameter of 9.5 cm. Subsequently, 300 ml of wash liquor containing 1.8 grams of the standard detergent were poured into the beaker and after the foam had disappeared, 25 mg of the agglomerates were evenly distributed over the surface of the liquid. After the agglomerates had reached the test fabric, it was left for 4 minutes. Next, the test fabric was transferred to a stop bath consisting of an aqueous solution of acetic acid (1%) and sodium bisulphate, after which it was dried and visually examined for pin point spotting (white spots on the test fabric). The results are shown in table 2. The data clearly show that the lauric acid coating of the present invention significantly reduces or eliminates the problem of pin point spotting with imidoperoxydicarboxylic acid bleaching agents.

Table 2: Effect of Coating (Agglomeration)

Composition PAP (wt.%) LA	100 0	75 25	60 40
Number of white spots on Sunak test fabric	214	110	0
Immidial Black	185	21	0

PAP = 6-phthalimido peroxyhexanoic acid

LA = Lauric acid

Example 5

Soaking Detergents

4 liters of wash liquor were prepared at 37° C including the following components:

Test Detergent IEC (6d g/l),

Enzyme Maxacal (110 mg/l),

5 Peroxy Acid (amount indicated in table 3).

The wash liquor was then poured into a tub with bottom dimensions of 30 x 40 cm. Test stains of 6 x 6 cm were applied to one half of a 40 x 40 cm kitchen towel and the test towel was placed in the wash liquor such that the stained half of the towel is covered by the unstained half of the towel. The wash was left overnight in the wash liquor and the next morning the towels were rinsed and dried. Finally, the reflectance
10 was measured by a standard procedure to determine the extent of stain removal. The results are given in table 3.

Table 3: Detergency of test formulations, expressed as
15 reflectance in %

Example		1	2	3	4	5
Bleach A.O. in ppm/		DPDA	PAP	PAP	-	H ₂ O ₂
Stain type Soil		30	20	30	0	100
25	bleachable red wine	71	71	73	49	52
	bleachable tea	70	70	70	51	52
	bleachable berries	71	70	74	44	45
30	enzymatic blood	37	53	46	67	29

35 Example 6

6-phthalimido peroxy hexanoic acid (PAP) as peroxy acid bleach granule

This example is to demonstrate the general feasibility of producing bleach granules.

Charged into a Eirich mixer were 430 g of an agglomerate of PAP and lauric acid (lauric acid: PAP
40 weight ratio 1:3 in filter cake form, water content 38.9%) and 266 g of completely dry PAP/lauric acid cake. Subsequently, there were added 10.7 g of a 50% paste of sodium dodecyl benzene sulphonate and the whole was mixed at 450 rpm and ambient temperature until a paste was formed. After 119 g of fine anhydrous sodium sulfate had been added, the whole was mixed at 48 rpm of the vessel and 450 rpm of the rotator at 30° C granules were formed.

45 The size of the granules obtained was in the range of about 1 mm to 2.0 mm.

Example 7

IPCA as a Bleaching Agent for Dishwashing Detergents used in Automatic Dishwasher

50 The compatibility of 6-phthalimidoperoxyhexanoic acid (PAP) was tested with two forms of standard materials used in dishwashing detergents for automatic dishwashers. First, two different sieve fractions of 0.4-0.8 mm of sodium metasilicate·5H₂O and of sodium disilicate hydrate were collected. To each of these sieve fractions were added 400 mg of bleach granules prepared in accordance with Example 6. The mixture of solids was then stored in an 800 ml glass jar with a pinhole in the screw top for an eight week period.
55 The glass jars were stored at 36.7° C and 32% relative humidity. The active oxygen contents of the materials were determined at 4 and 8 weeks by iodometric titration. The results are given in Table 4.

Comparative Example 2

The procedure of Example 7 was repeated except that DPDA was substituted for PAP in the granulate preparation process of Example 6. The results are also shown in Table 4.

Comparative Example 3

Example 7 and Comparative Example 2 were repeated using a solid standard textile detergent (IEC Detergent) instead of a dishwashing detergent. The results are shown in Table 4.

Table 4

Storage time in weeks	4		8	
Type of bleach	PAP	DPDA	PAP	DPDA
Initial A.O. in %	1.78	2.91	1.78	2.91
<u>Additive</u>				
No additive	100	91	90	87
Sodium metasilicate·5H ₂ O	96	81	81	71
Sodium disilicate hydrate	92	82	85	76
Textile (IEC) detergent	70	84	59	75

Example 7 and comparative examples 2 + 3 demonstrate that PAP is unexpectedly more compatible with silicates of dishwashing detergents than is DPDA. Further, the unexpectedness of this result is emphasized by the fact that DPDA is substantially more compatible with the textile detergent (IEC Detergent) than PAP.

Example 8

PAP and DPDA were granulated with sodium sulfate and tested for compatibility with dish washing detergents and one textile detergent. These granules were added to standard materials used in dish washing detergents as well as one textile detergent in the same manner as example 7 except that the PAP and DPDA were not coated with lauric acid. The mixture of solids was then stored in an 800 ml. glass jar with a pinhole in the screw top for 4 and 8 week periods. The glass jars were stored at 36.7° C and 32% relative humidity. The active oxygen contents of the materials were determined at 4 and 8 weeks by iodometric titration. The results are given in Table 5.

Table 5

5	Storage time in weeks	4		8	
	Type of bleach	PAP	DPDA	PAP	DPDA
	Initial A.O. in %	2.2	2.5	2.2	2.5
10	<u>Additive</u>				
	No additive	91	66	82	50
	Sodium metasilicate·5H ₂ O	95	--	87	--
15	Sodium disicate hydrate	99	--	92	--
	Soda ash	95	67	90	51
	Sodiumtripolyphosphate	94	--	86	--
20	Textile (IEC) detergent	90	57	80	27

These data show that the storage stability of PAP is not hindered and may even be slightly improved by highly alkaline dish washing detergents, whereas the storage stability of DPDA is clearly reduced by these same materials.

Example 9

In this example several different suspensions of PAP were prepared and stored for various periods to determine if PAP suspensions are storage stable. It was demonstrated that the suspensions are, in fact, storage stable for significant time periods of at least up to 26 weeks.

These suspensions were prepared by mixing the amounts of each ingredient as indicated in Table 6. The peroxy acid is first mixed with water and then the hydroxyethyl cellulose, thickening polymer, sodium sulfate and the sequestering agent were added. The chemical stability of the suspensions was measured at the times indicated in Table 6 and the results are shown in Table 6.

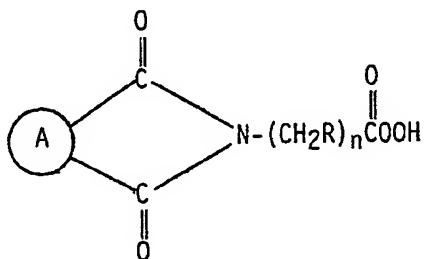
Table 6

Example	9a	9b	9c	9d
PAP in %	20	20	20	20
Thickening polymer type	Xanthan gum	Alpha flo®	Rhamsan gum	Welan® gum
content, %	0.2	2.5	0.15	0.20
Hydroxy ethyl cellulose	0.2	0.2	0.2	0.2
Na ₂ SO ₄	1.0	1.0	1.0	1.0
Dequest 2010	0.05	0.05	0.05	0.05
pH	3.5	3.5	3.5	3.5
Chemical Stability residual PAP in %				
4 weeks at 40°	93	--	94	93
8 weeks at 40°	85	88	88	88
26 weeks at room temperature	93	95	92	92

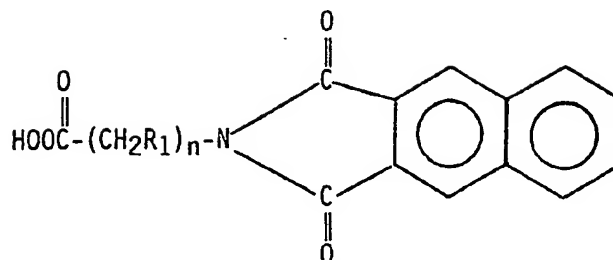
The foregoing examples have been presented for the purposes of illustration and description. The scope of the invention is to be determined by the claims appended hereto.

Claims

1. A pourable, aqueous bleaching composition comprising a suspended imidoperoxycarboxylic acid represented by the formula:



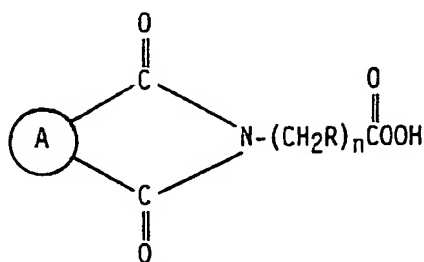
wherein A is a substituted or unsubstituted benzene ring or naphthalene ring, or



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$n=1-10$ and R and R_1 may be the same or different and are selected from hydrogen and a C_1-C_4 carboxylic acid radical, an alkali metal salt of an alkyl benzene sulphonc acid, and an inorganic salt.

2. A bleaching composition according to claim 1, characterized in that said bleaching composition comprises 0.5 to 40% by weight of said alkali metal salt of an alkyl benzene sulphonc acid, calculated on the weight of the bleaching composition.
3. A bleaching composition according to any one of claims 1 or 2, characterized in that said inorganic salt is a compound selected from the group consisting of sodium sulphate, potassium sulphate and mixtures thereof.
4. A bleaching composition according to any one of claims 1-3, characterized in that said inorganic salt is present in an amount of 0.01 to 35% by weight of the bleaching composition.
5. A bleaching composition according to any one of claims 1-4, characterized in that said bleaching composition further comprises a surfactant material.
6. A bleaching composition according to any one of claims 1-5, characterized in that said imidoperoxycarboxylic acid is ϵ -N,N-phthaloylaminoperoxycaproic acid.
7. Use as a pourable bleaching composition of a composition according to any one of claims 1-6.
8. A packaged bleaching composition, the bleaching composition being selected from compositions according to any one of claims 1-6.
9. A process for preparing coated agglomerates containing an imidoperoxycarboxylic acid represented by the following formula:



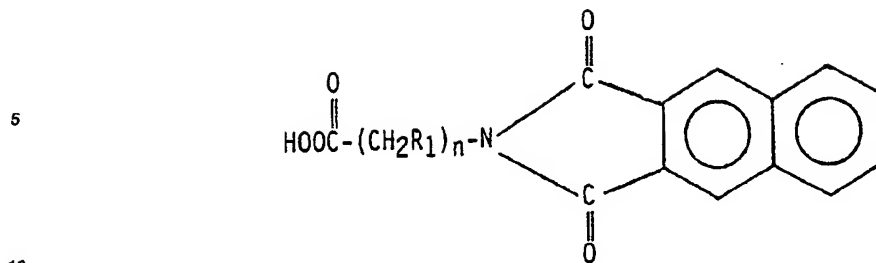
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wherein A is a substituted or unsubstituted benzene ring or naphthalene ring, or

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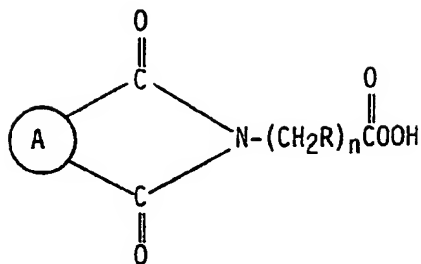


15 $n=1-10$ and R and R_1 may be the same or different and are selected from hydrogen and a C_1-C_4 carboxylic acid radical, and a water-impermeable material which is solid at room temperature, characterized in that the process comprises the steps of agitating an aqueous suspension of said acid in the presence of said water-impermeable material in an amount of at least 30% by weight, calculated on the acid, for a time sufficient to agglomerate the suspended acid particles and at a temperature above the melting point of said water-impermeable material and below the decomposition temperature of said acid, cooling with continued agitation of said suspension of the obtained agglomerated particles to a temperature at which said water-impermeable material solidifies, and isolating the resulting coated agglomerates.

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10. A process according to claim 9, characterized in that the amount of said water-impermeable material contained in said suspension is at most 100% by weight, calculated on said acid.
- 25 11. A process according to any one of claims 9 or 10, characterized in that said water-impermeable material is selected from the group of fatty acids having 10-20 carbon atoms, fatty alcohols having 14-20 carbon atoms and fatty acid esters.
- 30 12. A process according to claim 11, characterized in that said fatty acid is selected from the group consisting of lauric acid, myristic acid and a mixture thereof.
13. A process according to any one of claims 9-12, characterized in that said aqueous suspension is a suspension as claimed in any one of claims 1-6.
- 35 14. A process according to any one of claims 9-12, characterized in that said aqueous suspension is obtained by reacting an imidocarboxylic acid with hydrogen peroxide in aqueous media, in the presence of sulphuric acid, and, if necessary, diluting the resulting reaction mixture with water.
- 40 15. A process according to claim 14, characterized in that the sulphuric acid content is not more than 50% by weight, calculated on the total amount of sulphuric and water.
16. Shaped particles containing coated agglomerates obtained by any one of the methods claimed in claims 9-15 and further comprising a hydratable material.
- 45 17. A solid, particulate bleaching composition containing as a bleaching component a material selected from the group consisting of a coated agglomerate obtained by any one of the methods claimed in claims 9-15, and shaped particles as claimed in claim 16.
- 50 18. An aqueous, pourable bleaching composition or detergent and bleaching composition containing as a bleaching component a material selected from the group consisting of a coated agglomerate obtained by any one of the methods claimed in claims 9-15.
19. Use of an imidoperoxycarboxylic acid represented by the formula:

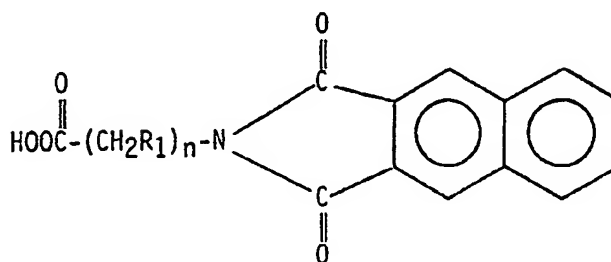
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wherein A is a substituted or unsubstituted benzene ring or naphthalene ring, or

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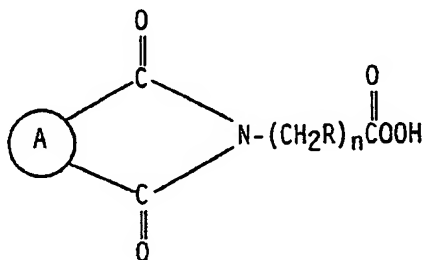
$n=1-10$ and R and R_1 may be the same or different and are selected from hydrogen and a C_1-C_4 carboxylic acid radical, as a bleaching component or an activator in a soaking detergent composition.

20. Use as claimed in claim 19, characterized in that said soaking detergent composition comprises at least one enzyme cleaning agent.

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21. A process for the cleaning of textile materials comprising the steps of soaking said textile materials for a period of at least four hours in an aqueous wash liquor which comprises water, a detergent composition and an imidoperoxycarboxylic acid represented by the formula:

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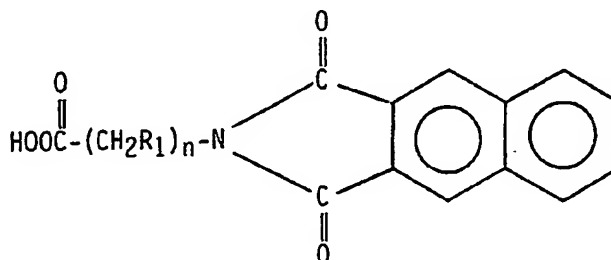


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wherein A is a substituted or unsubstituted benzene ring or naphthalene ring, or

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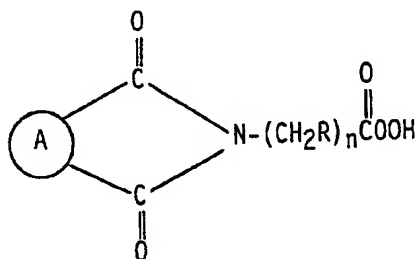
$n=1-10$ and R and R_1 may be the same or different and are selected from hydrogen and a C_1-C_4

carboxylic acid radical, and rinsing said textile materials.

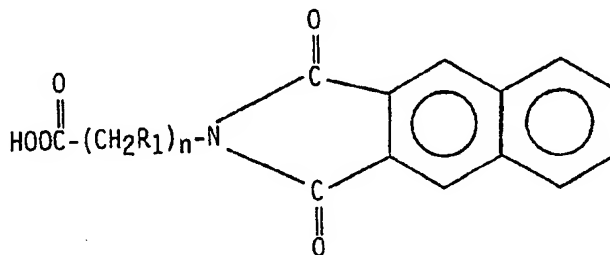
22. A process as claimed in claim 21, characterized in that said aqueous wash liquor further comprises an enzyme cleaning agent.

23. A process as claimed in any one of claims 21 or 22, characterized in that said imidoperoxycarboxylic acid is present in an amount sufficient to provide at least 5 ppm of active oxygen in said wash liquor.

24. A dishwashing detergent composition for automatic dishwashing machines including a dishwashing detergent component and further comprising a bleaching component containing at least one imidoperoxycarboxylic acid represented by the formula:



wherein A is a substituted or unsubstituted benzene ring or naphthalene ring, or



$n=1-10$ and R and R_1 may be the same or different and are selected from hydrogen and a C_1-C_4 carboxylic acid radical.

25. A process for washing dishes in an automatic dishwashing machine which comprises using a dishwashing detergent composition as claimed in claim 24.